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(71) Applicant (for all designated States except US): **UOP LLC** [US/US]; 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **TRAYNOR, Thomas** [US/US]; Uop Llc, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **BRANDVOLD, Timothy A.** [US/US]; Uop Llc, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(74) Agent: **PIASECKI, David J.**; Uop Llc, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

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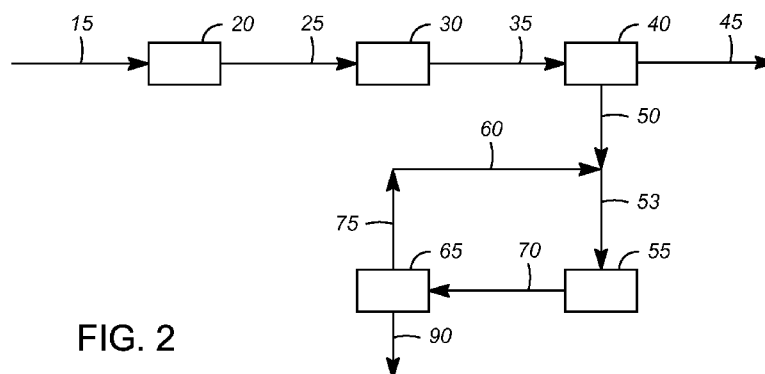


FIG. 2

(57) Abstract: Processes for producing a low acid biomass-derived pyrolysis oil are provided that include pre-treating a biomass-derived pyrolysis oil to form a treated acid-containing biomass-derived pyrolysis oil. The processes also include esterifying the treated acid-containing biomass-derived pyrolysis oil in the presence of supercritical alcohol and a catalyst composition to form the low-acid biomass-derived pyrolysis oil, the catalyst composition comprising a material selected from the group consisting of an unsupported solid acid catalyst, an unsupported solid base catalyst, and a catalytic metal dispersed on a metal oxide support.

PROCESSES FOR PRODUCING LOW ACID BIOMASS-DERIVED PYROLYSIS
OILS

STATEMENT OF PRIORITY

- 5 [0001] This application claims priority to U.S. Application No. 12/843,668 which was filed on July 26, 2010, the contents of which are hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

- 10 [0002] The present invention generally relates to biofuels and processes for producing biofuels, and more particularly relates to low acid biomass-derived pyrolysis oils and processes for producing the same.

DESCRIPTION OF RELATED ART

- 15 [0003] Biomass-derived pyrolysis oil can be burned directly as fuel for certain boiler and furnace applications, and can also serve as a potential feedstock in the production of biofuels in petroleum refineries or in stand-alone process units. To form biomass-derived pyrolysis oil, solid carbonaceous biomass feedstock, i.e., "biomass", such as wood waste, agricultural waste, etc., is initially rapidly heated to pyrolysis temperatures of 300°C to
20 900°C in the absence of air using a pyrolysis reactor. Under these conditions, solid products, liquid products, and gaseous pyrolysis products are produced. A condensable portion (vapors) of the gaseous pyrolysis products is condensed into biomass-derived pyrolysis oil.

- [0004] Although biomass-derived pyrolysis oil has great potential to replace up to 60%
25 of transportation fuels and to reduce the dependency on conventional petroleum and its environmental impact, unprocessed biomass-derived pyrolysis oil is a complex, highly oxygenated organic liquid having properties that currently limit its utilization as a biofuel. Specifically, unprocessed biomass-derived pyrolysis oil is generally thermally unstable and acidic (as measured by the total acid number (TAN)), making it corrosive, low in
30 energy density, and susceptible to increased viscosity over time. The low energy density and poor thermal stability of the biomass-derived pyrolysis oil is attributable in large part

“Oxygenated hydrocarbons” as used herein are organic compounds containing hydrogen, carbon, and oxygen. Such oxygenated hydrocarbons in the biomass-derived pyrolysis oil include carboxylic acids, phenols, cresols, aldehydes, etc. Conventional biomass-derived pyrolysis oil comprises 30% by weight oxygen from these oxygenated hydrocarbons.

5 [0005] Accordingly, it is desirable to provide methods for reducing the total acid number TAN of the biomass-derived pyrolysis oil to form low acid biomass-derived pyrolysis oils. It is also desirable to produce low acid biomass-derived pyrolysis oils having increased energy density, thermal stability and lower acidity. Furthermore, other desirable features and characteristics of the present invention will become apparent from
10 the subsequent detailed description of the invention and the appended claims, taken in conjunction with the accompanying drawings and this background of the invention.

SUMMARY OF THE INVENTION

[0006] Low acid biomass-derived pyrolysis oil and processes for producing the oils are
15 provided.

[0007] In an embodiment, by way of example only, a process for producing a low acid biomass-derived pyrolysis oil includes pre-treating a biomass-derived pyrolysis oil to form a treated acid-containing biomass-derived pyrolysis oil and esterifying the treated acid-containing biomass-derived pyrolysis oil in the presence of supercritical alcohol and a
20 catalyst composition to form the low-acid biomass-derived pyrolysis oil, the catalyst composition comprising a material selected from the group consisting of an unsupported solid acid catalyst, an unsupported solid base catalyst, and a catalytic metal dispersed on a metal oxide support. The unsupported solid acid catalyst comprises a material selected from the group consisting of a molecular sieve and a Group V metal oxide. The molecular
25 sieve comprises a material selected from the group consisting of zeolite and MCM 41. The unsupported solid base catalyst comprises a material selected from the group consisting of an alkaline earth metal exchanged molecular sieve, calcium oxide (CaO), magnesium oxide (MgO), and silicon oxide (SiO₂). The catalytic metal comprises a metal selected from the group consisting of noble metals, non-noble metals, and combinations
30 thereof. The metal oxide support comprises a metal oxide selected from the group consisting of a Group IV metal oxide, a Group V metal oxide, a Group IIIA metal oxide, and combinations thereof.

[0008] In another embodiment, by way of example only, a process for producing a low acid biomass-derived pyrolysis oil includes pre-treating a biomass-derived pyrolysis oil to form a treated acid-containing biomass-derived pyrolysis oil, diluting the treated acid-containing biomass-derived pyrolysis oil with supercritical ethanol to form a solution including at least 30% ethanol, by weight, and esterifying the treated acid-containing biomass-derived pyrolysis oil included in the solution in the presence of a catalyst composition and in the absence of gas in an upflow reactor to form the low-acid biomass-derived pyrolysis oil, wherein the catalyst composition comprises a noble metal support on a sulfated metal oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The present invention will hereinafter be described in conjunction with the following drawing figures, wherein like numerals denote like elements, and wherein:

[0010] FIG. 1 is a flow chart of a process for producing low acid biomass-derived pyrolysis oils, according to exemplary embodiments of the present invention;

[0011] FIG. 2 is a schematic diagram of the process of FIG. 1, according to exemplary embodiments of the present invention; and

[0012] FIG. 3 is a phase diagram for pure ethanol.

DETAILED DESCRIPTION

[0013] The following detailed description of the invention is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention.

Furthermore, there is no intention to be bound by any theory presented in the preceding background of the invention or the following detailed description of the invention.

[0014] Various exemplary embodiments of the present invention are directed to low acid biomass-derived pyrolysis oils and processes for producing the same. The low acid biomass-derived pyrolysis oils produced according to the present invention have lower total acid numbers ("TAN") as compared to biomass-derived pyrolysis oils produced by conventional processes. The processes comprise pre-treating a biomass-derived pyrolysis oil to form a treated acid-containing biomass-derived pyrolysis oil, and esterifying the treated acid-containing biomass-derived pyrolysis oil in the presence of supercritical ethanol and a catalyst composition to form the low-acid biomass-derived pyrolysis oil. It

should be appreciated that while the oil produced according to exemplary embodiments of the present invention is generally described herein as a “low acid biomass-derived pyrolysis oil”, this term generally includes any oil produced having a lower total acid number than conventionally-produced biomass-derived pyrolysis oil. The term “low acid biomass-derived pyrolysis oil” also includes oil having no acid species.

[0015] As shown in FIG. 1, in accordance with an exemplary embodiment, a process 100 for producing low acid biomass-derived pyrolysis oil begins by providing a treated acid-containing biomass-derived pyrolysis oil, step 102. As used herein, “treated acid-containing biomass-derived pyrolysis oil” comprises biomass-derived pyrolysis oil having a solids content less than 0.10 %, preferably less than 0.01 %; a total metals content of less than 100 ppm, preferably less than 20 ppm; and a water content of less than 20 weight percent (wt%), preferably less than 15 wt% (hereinafter referred to as “target levels”).

[0016] The treated acid-containing biomass-derived pyrolysis oil is provided by obtaining a starting conventional acid-containing biomass-derived pyrolysis oil or by forming an acid-containing biomass-derived pyrolysis oil. The starting conventional acid-containing biomass-derived pyrolysis oil may be obtained off-the-shelf, such as from, for example, Enslyn Technologies Inc., of Ontario, Canada. Typically, the conventional acid-containing biomass-derived pyrolysis oil contains 1000 to 2000 ppm total metals, 20-33 wt% water with high acidity (total acid number (TAN) > 150), and a solids content of 0.1 wt% to 5.0 wt%. In some cases, the conventional acid-containing biomass-derived pyrolysis oil may already have a solids content, a total metals content, and a water content at the desired target levels, the conventional biomass-derived pyrolysis oil may be used as the “treated acid-containing biomass-derived pyrolysis oil”. The starting conventional acid-containing biomass-derived pyrolysis oil may also be selectively treated to reduce only those levels not at the target level(s).

[0017] If formed, the acid-containing biomass-derived pyrolysis oil may be produced from fast pyrolysis of wood biomass in a pyrolysis reactor. However, virtually any form of biomass can be considered for pyrolysis to produce biomass-derived pyrolysis oil. In addition to wood, biomass-derived pyrolysis oil may be derived from biomass material such as bark, agricultural wastes/residues, nuts and seeds, algae, grasses, forestry residues, cellulose and lignin, or the like. The biomass-derived pyrolysis oil may be obtained by

different modes of pyrolysis, such as by fast pyrolysis, vacuum pyrolysis, catalytic pyrolysis, and slow pyrolysis (also known as carbonization) or the like.

[0018] The biomass employed for the pyrolysis process can be dried prior to entry into the pyrolysis reactor. For example, the biomass can be microwaved, oven-dried or the like to reduce an amount of water that is contained in the biomass. Alternatively or additionally, the biomass, dried or undried, is co-pyrolyzed with a material, such as an acid, suitable for removing oxygen from the pyrolysis gases formed during the pyrolysis process. In any case, the pyrolysis process yields the acid-containing biomass-derived pyrolysis oil. Although not specifically described, it will be appreciated that alternative methods for removing water can be employed.

[0019] To pre-treat the acid-containing biomass-derived pyrolysis oil or the starting conventional acid-containing biomass-derived pyrolysis oil, the oil is filtered to form a low-solids, acid-containing biomass-derived pyrolysis oil. For example, referring to FIG. 2, the acid-containing biomass-derived pyrolysis oil 15 may be, for example, filtered in a filtration apparatus 20 to substantially remove particulate solids therefrom to form low solids acid-containing biomass-derived pyrolysis oil 25. Filtration reduces a solids content of the acid-containing biomass-derived pyrolysis oil to the target levels to thereby prevent solids in the oil, which can include char and other insolubles, from plugging components. In addition, filtering the acid-containing biomass-derived pyrolysis oil increases the thermal stability of the resulting acid-containing biomass-derived pyrolysis oil produced in accordance with exemplary embodiments of the present invention as well as the thermal stability of the treated acid-containing biomass-derived pyrolysis oil produced by process 100. As used herein, "thermal stability" means the ability of the oil to resist changes in chemical composition and maintain phase stability as its temperature changes or with extended storage time. Filtration helps to lower viscosity, maintain homogeneity by improving phase stability, improve clarity, and increase pumpability of the oils produced in accordance with exemplary embodiments of the present invention.

[0020] The acid-containing biomass-derived pyrolysis oil is contacted with one or more filters (and filter media) for a selected period of time to produce a filtrate comprised of a low solids, acid-containing biomass-derived pyrolysis oil and a filter cake. The one or more filters may be used sequentially for treating the same volume of oil. The one or more filters may be of the same or different type using one or more of vacuum, gravity, or

pressure filtration. The filtrate is removed from the filter cake and the filtrate (the biomass-derived pyrolysis oil having increased thermal stability) is recovered. For pressure filtration, pressurized gas such as nitrogen, air, or the like may be supplied on the input side of the filter to accelerate filtration. Pressures (atm., absolute) from 1
5 atmosphere absolute pressure to 8 atmospheres absolute may be used. The period of time required for filtration is dependent on volume and viscosity of the oil being filtered, the amount and particle size of solids to be removed, the filter media (composition and pore size), and filtration pressure and temperature. For vacuum filtration, negative pressure (i.e., a vacuum) of 0.10 atm absolute to 0.95 atm absolute may be supplied on the output
10 side of the filter. No pressure is used for gravity filtration.

[0021] The filter may be comprised of a filter medium selected from the group consisting of nitrocellulose, cellulose acetate, glass fiber, polymeric (such as polytetrafluoroethylene and nylon-6), wire mesh, sintered metal, and the like, and can be provided in a variety of shapes and sizes. The filter medium preferably has a pore diameter
15 smaller than the char and other insolubles in the acid-containing biomass-derived pyrolysis oil. Filter pore diameters vary widely depending on the materials used, but typical pore diameters range from 0.1 to 100 micrometers. Preferred pore diameters range from 5 to 50 micrometers. Exemplary filter/filter medium and filtration equipment suppliers include Whatman Plc (Kent, U.K.), Millipore Corporation (Billerica, MA), Filtrex Corporation
20 (Attleboro, MA), Mott Corporation (Farmington, CT) and Pall Corporation (Port Washington, NY). As used herein, "low solids" includes zero solids. Solids content in biomass-derived pyrolysis oil may be measured as described in the Annex to ASTM D7544-09 "Standard Specification for Pyrolysis Liquid Biofuel", or by other known methods.

[0022] Optionally, a total metal concentration of the acid-containing biomass-derived pyrolysis oil is reduced to target levels to form a low solids, low metal, acid-containing biomass-derived pyrolysis oil. In this regard, the acid-containing biomass-derived
25 pyrolysis oil 25, whether filtered or unfiltered, is subjected to an ion-exchange process 30. Specifically, an ion-exchange material having acidic active sites can be used to cause
30 metals in the acid-containing biomass-derived pyrolysis oil to preferentially migrate out of the oil to the acidic active sites on the ion-exchange material. The metals in the acid-containing biomass-derived pyrolysis oil are replaced by hydrogen ions.

[0023] The ion-exchange can be accomplished by either a batch method or a continuous column method. In the batch method, the ion-exchange material and starting acid-containing biomass-derived pyrolysis oil (which may or may not be low solids) are contacted by mixing the ion-exchange material and starting oil in a vessel, batch tank, or the like. A given weight of ion-exchange material is added to a known volume of starting acid-containing biomass-derived pyrolysis oil. The amount of ion-exchange material added to the fixed amount of oil is typically an excess of the ion-exchange material (based on theoretical material capacity, as defined below). The optimum material to oil ratio is determined experimentally and is impacted by temperature and exposure time. The material/oil mixture is agitated for 0.5 hours to 24 hours, preferably 0.5 to 4 hrs (hereinafter "the exposure time") at a temperature of 10°C to 120°C, preferably from 20°C to 60°C. Samples of the treated oil may be collected and analyzed for metal content, as hereinafter described.

[0024] In the continuous column method, the ion-exchange material and the acid-containing biomass-derived pyrolysis oil are contacted by passing the biomass-derived pyrolysis oil through a column (of one or more "beds") containing the ion-exchange material. The material temperature may be from 10°C to 120°C, preferably from 20°C to 60°C. The acid-containing biomass-derived pyrolysis oil is passed through the column by positive pressure flow or by gravity flow. When pressure is applied, the absolute pressure is from greater than 0 KPa to 13790 KPa (0 to 2000 psi), preferably from greater than 0 KPa to 689.5 KPa (greater than 0 psi to 100 psi), and most preferably from 13.8 KPa to 206.8 KPa (2 psi to 30 psi). When no pressure is applied, the acid-containing biomass-derived pyrolysis oil has a reduced total metal content and passes downward through the column to slowly elute gravimetrically.

[0025] The acid-containing biomass-derived pyrolysis oil is passed over the ion-exchange material at a Liquid Hourly Space Velocity (LHSV) of 0.1-20 hr⁻¹, preferably 1-10 hr⁻¹. The faster the LHSV, the less time there is for ion-exchange to occur. When the LHSV is reduced, the concentration of the selected metal ions in the treated oil is reduced significantly.

[0026] When metal levels in the treated acid-containing biomass-derived pyrolysis oil reach a target concentration, or when metal concentration is constant (as determined by repeat measurements) over an extended time period, contact between the oil and the resin

may be concluded and ion-exchange is deemed “complete”. Metal concentrations in the oil may be measured by Atomic Absorption Spectroscopy (AAS), Inductively-Coupled Plasma- Atomic Absorption Spectroscopy (ICP-AAS) or other known methods.

[0027] The volume capacity of the ion-exchange material (VC_r) for both batch and continuous column methods is the volume of material needed to completely ion-exchange a given mass of oil and is determined by the equation:

$$VC_r (\text{mL material /kg oil}) = (\sum_i (C_i * 1000 \text{ g/kg}) / MW_i) * V_i * 1000 \text{ meq/eq} / (TC_r * D_r)$$

10 wherein:

C_i is the concentration of metal i in the biomass-derived pyrolysis oil in gram metal/gram oil;

MW_i is the molecular weight of metal in g/mol;

V_i is the valency (charge) of metal i in solution;

15 D_r is the ion-exchange material density in g/mL; and

TC_r is the theoretical capacity of ion exchange material r . Theoretical capacity (TC_r) is often expressed in terms of milliequivalents ions/gram ion exchange material.

[0028] The maximum volume of oil (in liters) that can be processed per unit volume of ion-exchange material in both batch and continuous column methods is expressed as:

20 $V_{oil} = V_r / (VC_r * D_{feed})$

wherein:

V_{oil} is the volume of low solids biomass-derived pyrolysis oil in liters;

D_{feed} is the feed oil (the starting biomass-derived pyrolysis oil) density (in kilograms/liter);

V_r is the material volume in milliliters; and

25 VC_r is the volume capacity of acidic ion-exchange resin to a given mass of metal-containing acid-containing biomass-derived pyrolysis oil as determined above and expressed in mL ion exchange material /kg of biomass-derived pyrolysis oil. The V_{oil}/V_r processed is also known as the number of bed volumes (BV) of oil processed. For a continuous column method, the volume of ion-exchange material is fixed and a sub-theoretical volume of oil is passed through the ion-exchange material. Filtered biomass-derived pyrolysis oil is contacted with 0.1 to 10 times the volume capacity (VC_r) of the acidic ion-exchange material, preferably 1 to 5 VC_r .

30

[0029] Ion exchange material efficiency, also referred to as ion-exchange efficiency (IX_{eff}), is defined as the fraction of metals removed from the liquid biomass-derived pyrolysis oil relative to the theoretical capacity of the ion exchange material and is determined as follows:

$$5 \quad IX_{eff} = (\sum((C_{if}-C_{ip}) * V_i / MW_i * 1000 * M_f)) / (TC_r * M_r),$$

where C_{if} and C_{ip} are the concentration of metal i expressed in terms of grams of metal i per gram of oil in the feed (biomass-derived pyrolysis oil) and product (low metal biomass derived pyrolysis oil), respectively, M_f is the mass of feed oil in grams, MW_i is the molecular weight of metal i in g/mol, V_i is the valency (charge) of metal i in solution, TC_r is the theoretical capacity of ion exchange material r and M_r is the mass in grams of ion exchange material r utilized. If it is assumed that a single metal ion neutralizes one ion exchange material exchange site regardless of ion charge, then the valence of the individual ions (V_i) is assigned as 1 for all metals. A higher exchange efficiency is typically desired. Theoretical ion exchange material capacity multiplied by the ion exchange efficiency provides the actual capacity, which is the amount of ion-exchange material needed to actually deionize a given amount of acid-containing biomass-derived pyrolysis oil. The lower the experimental material capacity, i.e., the lower the concentration of acid sites (eq/L), the larger the column needs to be, i.e., the greater the material volume needed to deionize the filtered acid-containing biomass-derived pyrolysis oil.

[0030] Suitable ion-exchange resins useful in this process are strongly acidic cation-exchange resins can be employed. Preferably, the resin is used in the protonated form, i.e., all of the active groups are $-SO_3H$. Neutralized sulfonic acid resins, in which some or all of the protons have been exchanged by a cation such as lithium, sodium, potassium, magnesium, and calcium are also suitable. However, if resins are supplied with an alternate counterion (i.e., sodium, Na^+), then the acid form may be generated prior to use by treatment with aqueous acid (such as hydrochloric, nitric, or sulfuric acid, etc.) This is commonly known in the art as ion-exchange resin activation. Preferably, the resin comprises sulfonated copolymers of styrene.

[0031] Preferred sulfonic acid resins are macroreticular resins. As used herein, "macroreticular resins" are made of two continuous phases—a continuous pore phase and a continuous gel polymeric phase. The continuous gel polymeric phase is structurally

composed of small spherical microgel particles agglomerated together to form clusters, which, in turn, form interconnecting pores. The surface area arises from the exposed surface of the microgel clusters. Macroreticular ion exchange resins can be made with different surface areas ranging from 7 to 1500 m²/g, and average pore diameters ranging from 5 to 10000 nm.

[0032] Gel-type resins may also be used. As used herein, "gel-type resins" are generally translucent. There are no permanent pore structures for the gel-type resins. The pores are generally considered to be molecular-scale micropores. The pore structures are determined by the distance between the polymer chains and crosslinks which vary with the crosslink level of the polymer, the polarity of the solvent, and the operating conditions.

Macroreticular resins are preferable for continuous column ion-exchange applications where resin swelling/shrinking should be minimized, while gel-type resins are preferred for batch ion-exchange applications, but either type may be used in either application.

[0033] Exemplary suitable acidic ion-exchange resins include those manufactured by

Dow Chemical Co., Midland, MI (USA) under the tradenames/trademarks DOWEX® MARATHON C, DOWEX® MONOSPHERE C-350, DOWEX® HCR-S/S, DOWEX® MARATHON MSC, DOWEX® MONOSPHERE 650C, DOWEX® HCR-W2, DOWEX® MSC-1, DOWEX® HGR NG (H), DOWEX® DR-G8, DOWEX® 88, DOWEX® MONOSPHERE 88, DOWEX® MONOSPHERE C-600 B, DOWEX® MONOSPHERE M-31, DOWEX® MONOSPHERE DR-2030, DOWEX® M-31, DOWEX® G-26 (H), DOWEX® 50W-X4, DOWEX® 50W-X8, DOWEX® 66, those manufactured by Rohm and Haas, Philadelphia, PA (USA) under the tradenames/trademarks Amberlyst® 131, Amberlyst® 15, Amberlyst® 16, Amberlyst® 31, Amberlyst® 33, Amberlyst® 35, Amberlyst® 36, Amberlyst® 39, Amberlyst® 40 Amberlyst® 70, Amberlite® FPC11, Amberlite® FPC22, Amberlite® FPC23, those manufactured by Brotech Corp., Bala Cynwyd, PA (USA) under the tradenames/trademarks Purolite® PFC150, Purolite® C145, Purolite® C150, Purolite® C160, Purolite® PFC100, Purolite® C100, and those manufactured by Thermax Limited Corp., Novi, MI (USA) under the tradename/trademark Monoplus™ S100 and Tulsion® T42.

[0034] The low metal, acid-containing biomass derived pyrolysis oil having the target level of total metals of less than 100 ppm, preferably less than 20 ppm is produced from

ion-exchange. Conventional acid-containing biomass-derived pyrolysis oil may be a low metal acid-containing biomass-derived pyrolysis oil if the total metals content therein is already at the target total metals level. As used herein, "low metals" includes zero metals. The low metal acid-containing biomass-derived pyrolysis oil (which may or may not be low solids) is then removed from the used ion-exchange resin (hereinafter "spent ion-exchange resin"). In a batch ion-exchange, the low metal acid-containing biomass-derived pyrolysis oil may be removed by filtration, decantation, or other known method. In continuous column ion exchange, the low metal acid-containing biomass-derived pyrolysis oil is removed from the spent ion-exchange resin when the low metal acid-containing biomass-derived pyrolysis oil elutes from the column gravimetrically or under positive pressure. While particular ion-exchange methods have been described, other methods of reducing the total metal content to the target level may be used in accordance with exemplary embodiments of the present invention.

[0035] In another optional embodiment of step 102, the acid-containing biomass-derived pyrolysis oil (which may or may not be low solids or low metal) may be subjected to a water reduction process. For example, the acid-containing biomass-derived pyrolysis oil may be subjected to an azeotropic, vacuum, gas-assisted, or atmospheric distillation process in a first fractionator such as a distillation apparatus to remove at least a portion of the water therein to reduce the water content therein. Azeotropic, vacuum, and gas-assisted distillation processes permit the removal of water from acid-containing biomass-derived pyrolysis oil without having to heat the oil to at least 100°C (the boiling point of water at one atmosphere) to remove the water, i.e., such processes allow atmospheric distillation at lower temperatures. The use of lower temperatures to remove the water from the oil substantially prevents solidification (phase separation) and/or solidification of the oil that is experienced at elevated temperatures (typically 150°C).

[0036] Vacuum distillation is performed at lower than atmospheric pressure to lower the boiling point of the water in the acid-containing biomass-derived pyrolysis oil so that water therein may be removed by heating the acid-containing biomass-derived pyrolysis oil at least to the lower boiling point of water at that reduced pressure. The boiling point of water at that pressure may be determined by consulting temperature/pressure charts that are available from, for example, the National Bureau of Standards (NBS)/National Research Council (NRC). Vacuum may be applied by a vacuum pump, aspirator, or the

like. In a preferred embodiment, the acid-containing biomass-derived pyrolysis oil is heated to 65°C at a vacuum of 0.05 to 0.95 atm (absolute pressure) until the desired amount of water is removed to reach the target level.

[0037] Gas-assisted distillation uses a standard distillation column with an inert gas such as nitrogen, air, argon, helium, hydrogen or other gas passing into and over the low metal, acid- and water-containing biomass-derived pyrolysis oil while heating the low metal biomass-derived pyrolysis oil to a selected temperature of 30°C to 90°C, preferably 70°C at a flow rate of 0.1 to 100 liters (L) gas/L oil/minute, preferably 0.5 to 4 L gas/L oil/min. Gas-assisted distillation functionally reduces the vapor pressure of the oil, thus resulting in more water in vapor phase so that it can be removed from the low metal acid-containing biomass-derived pyrolysis oil at less than 100°C. The rate at which the water is removed is limited by the vapor pressure of water at the selected temperature, the gas flow rate, and the liquid volume to be distilled. The gas flow rate (controlled by a mass flow controller or valve) and selected temperature may be varied depending on the desired rate of water removal. The wt% water in the starting and treated biomass-derived pyrolysis oil may be measured, for example, by Karl Fischer Reagent Titration Method (ASTM D1364) as known to one skilled in the art. Preferably, the treated biomass-derived pyrolysis oil contains less than 20 weight percent water (the “target level”).

[0038] While particular methods for reducing the water content in acid-containing biomass-derived pyrolysis oil have been described, other methods of reducing water in biomass-derived pyrolysis oil known to those skilled in the art may be used. It is also noted that while ion-exchange prior to water removal has been described, metal removal (including ion-exchange) following water removal may also be performed (not shown). As a result of fractionation in the first fractionator, a “low water acid-containing biomass derived pyrolysis oil” 50 having the target level of water of less than 20 weight percent (wt%), preferably less than 15 wt% is produced. As used herein, “low water” includes zero water.

[0039] As a result of reducing one or more of the solids, and/or the total metal content, and/or the water content, the acid-containing biomass-derived pyrolysis oil is transformed to the treated acid-containing biomass derived pyrolysis oil comprising solids, metal, and/or water content at the target levels.

[0040] The treated acid-containing biomass-derived pyrolysis oil is esterified in the presence of supercritical alcohol to form the low-acid biomass-derived pyrolysis oil, step 104. The treated acid-containing biomass-derived pyrolysis oil 50 is diluted with the alcohol 60 to form a solution 53. The alcohol 60 employed for esterification includes, but is not limited to aliphatic alcohols, such as methanol, ethanol, propanol, and butanol.

[0041] Diluting can be achieved by placing a predetermined volume of the treated acid-containing biomass-derived pyrolysis oil in a container, such as a tank, vessel or the like, and adding the ethanol to the container to form the solution. In an example, an amount of ethanol is added to the treated acid-containing biomass-derived pyrolysis oil such that the solution 53 includes at least 15% alcohol by weight. In other embodiments, more or less alcohol is added to the solution.

[0042] The solution 53 is esterified at a temperature and a pressure that are at supercritical or just below critical limitations (e.g., within 10% of critical temperature and pressure) of the alcohol. For example, esterification can be performed at a temperature in a range of 180°C to 290°C at a pressure of at least 4.41 MPa (640 psi) to 8.00 MPa (1160 psi). In other embodiments, the particular temperatures and/or pressures employed are selected based on the alcohol included in the solution 53. In any case, the solution is esterified for a residence time in a range of 0.5 hour to 3 hours. In other embodiments, esterification occurs for a longer or shorter time period. Esterification preferably occurs in the absence of gas. In this regard, an inert gas, such as nitrogen, can be employed to evacuate the atmosphere in which esterification occurs, and a vacuum seal may be formed after the atmosphere is substantially completely evacuated.

[0043] The solution 53 is passed through a reactor 55 under supercritical conditions or near critical conditions (e.g., +/- 10% of the critical temperature and the pressure) of alcohol to esterify the acids in the solution 53. As used herein, the term “supercritical conditions” is defined as a temperature and pressure above a critical point of the alcohol. FIG. 3 is a phase diagram for pure ethanol. The phase diagram includes an x-axis 302 representing temperature as measured in °C and a y-axis 304 representing pressure as measured in megaPascals (MPa). Line 306 includes a triple point 308 from which another line 310 extends to thereby indicate a phase change threshold between the solid, liquid, and vapor phases of ethanol. Line 306 further includes a critical point 312 at which the liquid and gaseous phase of ethanol become substantially identical. The critical point 312

for ethanol is at 243°C and 6.38 MPa (925 psi). As shown in FIG. 3, points along line 306 beyond the critical point 312 correspond to supercritical conditions. Other aliphatic alcohols employed during esterification have critical points that are different from that of ethanol. For example, the critical point of methanol is at 240°C and 7.95 MPa (1153 psi).
5 The critical point of propanol is at 268.6°C and 5.16 MPa (749 psi), and the critical point of butanol is at 289.8°C and 4.42 MPa (641 psi).

[0044] The reactor is an upflow tubular reactor with or without a fixed catalyst bed. Although the preferred reactor comprises the upflow tubular reactor, downflow reactors can be employed in some embodiments. Suitable types of reactors include, but are not
10 limited to fluidized bed systems, batch reactors, continuously stirred reactors, and the like. No matter the particular type of reactor employed, the catalyst composition can be simply placed within the reactor or on the catalyst bed for reaction with the solution.

[0045] According to an embodiment, esterification is performed in the absence of a catalyst composition. In accordance with another embodiment, esterification is performed
15 in the presence of a catalyst composition. As used herein, a “catalyst composition” is defined as solid composition comprising at least an active phase. The catalyst composition is selected to reduce the total acid number of the acid-containing biomass-derived pyrolysis oil. In this regard, suitable catalyst compositions comprise materials such as solid acid catalysts, solid base catalysts or catalytic metals dispersed on a solid support
20 such as those typically employed for hydroprocessing. Exemplary solid acid catalysts include, but are not limited to, molecular sieves, metal oxides, and sulfated metal oxides. Suitable molecular sieves include, but are not limited to materials such as zeolites and MCM 41. The zeolite can be selected from BEA-type zeolites, zeolite X, zeolite Y, zeolite ZSM 5, and zeolite ZSM 12. Metal oxides useful as solid acid catalysts include
25 those selected from Group IV metal oxides and Group V metal oxides. For example, Group IV metal oxides include, but are not limited to titanium oxide (TiO₂) and zirconium oxide (ZrO₂). Group V metal oxides include niobium oxide (Nb₂O₅). In other embodiments, other Group IV and V metal oxides and combinations thereof can alternatively be employed. Sulfated metal oxides used as solid acid catalysts include
30 sulfated zirconia. The aforementioned solid acid catalysts are intended for use as standalone catalysts. Hence, the solid acid catalyst is not employed with a support material (e.g., is an unsupported solid acid catalyst).

[0046] The solid base catalysts include, but are not limited to basic metal oxides and alkaline-earth metal exchanged molecular sieves. Suitable basic metal oxides employed as solid base catalysts include, but are not limited to calcium oxide (CaO), magnesium oxide (MgO), silicon oxide (SiO₂), and other basic metal oxides. Exemplary alkaline-earth metal exchanged molecular sieves suitable for inclusion as the catalyst composition include, but are not limited to, barium exchanged molecular sieves, calcium exchanged molecular sieves, and the like. The aforementioned solid base catalysts are intended for use as standalone catalysts. Hence, the solid base catalyst is not employed with a support material (e.g., is an unsupported solid base catalyst).

[0047] In other embodiments, the catalyst composition may comprise one or more metals dispersed on a metal oxide support. The metal may be dispersed on the support as the oxide, sulfide or as the metal (zero valent state). Examples of supported catalyst compositions which may be used are those employed for hydroprocessing. For example, the catalytic metals can comprise one or more noble metals or non-noble metals. In an embodiment, the noble metal may be present in an amount from 0.1 wt% to 1.5 wt of the catalyst composition. As used herein, "wt%" means the weight of the catalytic metal (as the metal) divided by the total weight of the catalytic composition (catalytic metal weight plus weight of the support). Suitable noble metals include, but are not limited to gold (Au), platinum (Pt), rhodium (Rh), ruthenium (Ru), palladium (Pd), iridium (Ir), and combinations thereof.

[0048] If a non-noble metal is used, they can be selected from nickel (Ni), cobalt (Co), molybdenum (Mo), tungsten (W), and combinations thereof. For example, metals such as Ni/Mo, Co/Mo, Ni/Co/Mo, Ni/W, and combinations thereof, may be employed. If the catalytic metals are Ni/Mo, the metals may be present in an amount from 0.5 wt% to 3.5 wt% of nickel, and 5 wt% to 20 wt% of molybdenum. In an embodiment in which Co/Mo are the catalytic metals, the metals may be present from 0.5 wt% to 3.5 wt% of cobalt and 5 wt% to 20 wt% of molybdenum. If Ni/Co/Mo are the catalytic metals, the metals may be present from 0.1 wt% to 1.5 wt% of nickel, 0.5 wt% to 3.5 wt% of cobalt, and 5 wt% to 20wt% of molybdenum. For the case of Ni/W, the metal concentration is 0.5 wt% to 3.5 wt% of nickel and 5 wt% to 20 wt% of tungsten.

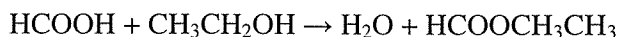
[0049] If employed, the support materials include metal oxide support materials, including, but not limited to a Group IV metal oxide, a Group V metal oxide, and a Group

IIIA metal oxide. The metal oxide support can be selected from a group consisting essentially of titanium oxide (TiO₂), zirconium oxide (ZrO₂), niobium oxide (Nb₂O₅), quartz, silicon carbide, aluminum oxide (Al₂O₃), silicon oxide (SiO₂), and combinations thereof.

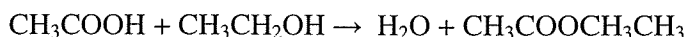
5 [0050] In another embodiment, the catalyst composition comprises a sulfated metal oxide. For example, the sulfated metal oxide comprises sulfated zirconia. The sulfated metal oxide can support a metal, in an embodiment. In an example, the metal is a noble metal. In such case, the noble metal comprises palladium.

[0051] As a result of esterification, the acids in the biomass-derived pyrolysis oil are
 10 converted into esters to thereby yield a low acid biomass-derived pyrolysis oil 70. For example, light carboxylic acids (e.g., acids having C₁-C₄) are converted to volatile esters. As used herein, "volatile esters" have a boiling point below or equal to the normal boiling point of the ethanol. In some cases, 80% to 95% of the light carboxylic acids are converted, thereby reducing the TAN of the biomass-derived pyrolysis oil by 5% by
 15 weight. Exemplary equations of the reactions that may occur within the biomass-derived pyrolysis oil are provided below.

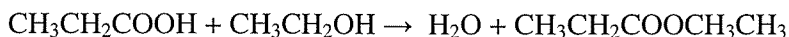
Formic Acid + Ethanol → Water + Ethyl Formate



20 Acetic acid + Ethanol → Water + Ethyl Acetate

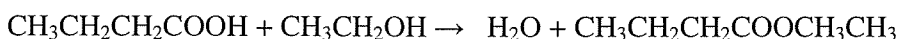


Propionic Acid + Ethanol → Water + Ethyl Propionate



25

Butanoic Acid + Ethanol → Water + Ethyl Butyrate



[0052] Optionally, after esterification, the low acid biomass-derived pyrolysis oil 70
 30 may undergo fractionation 65 to remove ethanol 75, step 106. The removed ethanol 75 can be recycled and returned to the reactor for use as the supercritical ethanol in later esterification steps. The remaining low acid biomass-derived pyrolysis oil, now

comprising volatile esters forms treated biomass-derived pyrolysis oil 90. Fractionation can be achieved by providing a temperature gradient along a fractionation column, where a minimum temperature of the temperature gradient is set just above the boiling point of ethanol. A fraction of the low acid biomass-derived pyrolysis oil (e.g., the ethanol) is collected at a location along the temperature gradient, distilled and directed to a separate container. While TAN reduction using esterification with an esterification catalyst and supercritical ethanol has been described, the total acid number (inclusive of the carboxylic acid number) may be further reduced by other methods known in the art, including but not limited to other esterification methods.

[0053] The following examples are not intended to limit the invention in any way and are merely presented to illustrate the improved process for producing the low acid biomass-derived pyrolysis oil described above.

Example 1

[0054] A pre-blended feed was prepared for use in several experiments, as will be discussed in further detail below. The pre-blended feed included 50 weight percent (wt%) ethanol and 50 wt% low water biomass-derived pyrolysis oil. The blended feed had a total acid number (TAN) of 110.5, where 40.9 of the TAN was attributed to carboxylic acid and 69.6 of the TAN was attributed to phenolic.

Example 2

[0055] One hundred (100) grams of the pre-blended feed was added to an autoclave including 5.0 grams of 0.5% platinum on γ alumina. A head pressure of nitrogen 2.75 MPa (400 psig) was added to the autoclave. The autoclave was then heated to a temperature in a range of 255°C. The temperature was maintained for 1.8 hours, and a maximum pressure of 12.41 MPa (1800 psig) was achieved to provide supercritical conditions for the ethanol and to esterify the oil in the pre-blended feed. After the reaction, the pressure at room temperature was 4.13 MPa (600 psig). No solids were found in the autoclave, and 10 grams of the liquid was converted to gas. The TAN of the esterified feed was 65.62, where 25.24 of the TAN was attributed to carboxylic acid and 40.38 of the TAN was attributed to phenolic.

Example 3

[0056] Ninety (90) grams of the pre-blended feed was added to an autoclave including 4.5 grams of 70% to 85% silicon oxide and 15% to 30 % aluminum oxide. A head pressure of nitrogen in a range of 2.75 MPa (400 psig) was added to the autoclave. The autoclave was then heated to a temperature in a range of 255°C. The temperature was maintained for 1.8 hours, and a maximum pressure of 1800 psig was achieved to provide supercritical conditions for the ethanol and to esterify the oil in the pre-blended feed. After the reaction, the pressure at room temperature was 3.79 MPa (550 psig). No solids were found in the autoclave, and 6% of the liquid was converted to gas. The TAN of the esterified feed was 64.5, where 22.43 of the TAN was attributed to carboxylic acid and 42.06 of the TAN was attributed to phenolic.

Example 4

[0057] One hundred (100) grams of the pre-blended feed was added to an autoclave including 5.0 grams of magnesium oxide (MgO). A head pressure of nitrogen in a range of 2.75 MPa (400 psig) was added to the autoclave. The autoclave was then heated to a temperature in a range of 255°C. The temperature was maintained for 2.0 hours, and a maximum pressure of 11.03 MPa (1600 psig) was achieved to provide supercritical conditions for the ethanol and to esterify the oil in the pre-blended feed. 40 % solids were found in the autoclave. The TAN of the esterified feed was 55.2.

Example 5

[0058] One hundred forty (140) grams of the pre-blended feed was added to an autoclave including 3.5 grams of sulfonic acid washed carbon. A head pressure of nitrogen in a range of 3.10 (MPa) 450 psig was added to the autoclave. The autoclave was then heated to a temperature in a range of 263°C. The temperature was maintained for 2.0 hours, and a maximum pressure of 13.27 MPa (1925 psig) was achieved to provide supercritical conditions for the ethanol and to esterify the oil in the pre-blended feed. 28 % solids were found in the autoclave. The TAN of the esterified feed was 38.6.

Example 6

[0059] A pre-blended feed of 50 wt% ethanol and 50 wt% of a low metal, low water, low solids biomass-derived pyrolysis oil (e.g., having metal, water, and solid contents within the aforementioned target values) was prepared. The TAN of the pre-blended feed was measured as 132.7.

Example 7

[0060] A pre-blended feed having a composition similar to that of the pre-blended feed in Example 6 was fed through a tubular reactor filled with quartz chips at a liquid flow rate of 75 cc per hour. The reactor was heated to a temperature of 260°C and held at a maximum pressure of 10.34 MPa (1500 psig) to esterify. A yield loss of 94% was measured and attributed to carbon monoxide/carbon dioxide formation. A TAN of the esterified feed was measured to be 77.8.

Example 8

[0061] A pre-blended feed having a composition similar to that of the pre-blended feed in Example 6 was fed through a tubular reactor filled with quartz chips at a liquid flow rate of 75 cc per hour. The reactor was heated to a temperature of 228°C and held at a maximum pressure of 10.34 MPa (1500 psig) to esterify. A yield loss of 96% was measured and attributed to carbon monoxide/carbon dioxide formation. A TAN of the esterified feed was measured to be 82.2.

Example 9

[0062] A pre-blended feed having a composition similar to that of the pre-blended feed in Example 6 was fed through a tubular reactor filled with quartz chips at a liquid flow rate of 75 cc per hour. The reactor was heated to a temperature of 280°C and held at a maximum pressure of 10.34 MPa (1500 psig) to esterify. A yield loss of 93% was measured and attributed to carbon monoxide/carbon dioxide formation. A TAN of the esterified feed was measured to be 66.7.

Example 10

[0063] A pre-blended feed having a composition similar to that of the pre-blended feed in Example 6 was fed through a tubular reactor filled with quartz chips at a liquid flow rate of 75 cc per hour. The reactor was heated to a temperature of 260°C and held at a maximum pressure of 10.34 MPa (1500 psig) to esterify. A yield loss of 94% was measured and attributed to carbon monoxide/carbon dioxide formation. A TAN of the esterified feed was measured to be 71.1.

Example 11

10 [0064] A pre-blended feed having a composition similar to that of the pre-blended feed in Example 6 was fed through a tubular reactor filled with alpha alumina at a liquid flow rate of 75 cc per hour. The reactor was heated to a temperature of 260°C and held at a maximum pressure of 10.34 MPa (1500 psig) to esterify. A yield loss of 94% was measured and attributed to carbon monoxide/carbon dioxide formation. A TAN of the esterified feed was measured to be 99.8.

Example 12

[0065] A pre-blended feed having 10 wt% ethanol and 90 wt% low metal, low water biomass-derived pyrolysis oil was fed through a tubular reactor filled with alpha alumina at a liquid flow rate of 75 cc per hour. The reactor was heated to a temperature of 260°C and held at a maximum pressure of 10.34 MPa (1500 psig) to esterify. A yield loss of 96% was measured and attributed to carbon monoxide/carbon dioxide formation. A TAN of the esterified feed was measured to be 178.5.

25 [0066] Processes have now been provided for reducing the total acid number of the biomass-derived pyrolysis oil to form low acid biomass-derived pyrolysis oils. The low acid biomass-derived pyrolysis oils produced by the above-described processes have increased energy density, thermal stability and lower acidity, as compared to conventionally-produced biomass-derived pyrolysis oil. Moreover, the processes described above are relatively inexpensive and simple to implement.

30 [0067] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of

variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for

5 implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims and their legal equivalents.

CLAIMS

What is claimed is:

1. A process for producing a low-acid biomass-derived pyrolysis oil
5 comprising:
pre-treating a biomass-derived pyrolysis oil to form a treated acid-containing biomass-derived pyrolysis oil; and
esterifying the treated acid-containing biomass-derived pyrolysis oil in the presence of supercritical alcohol and a catalyst composition to form the low-acid biomass-
10 derived pyrolysis oil, the catalyst composition comprising a material selected from the group consisting of an unsupported solid acid catalyst, an unsupported solid base catalyst, and a catalytic metal dispersed on a metal oxide support, wherein:
the unsupported solid acid catalyst comprises a material selected from the group consisting of a molecular sieve and a Group V metal oxide,
15 the molecular sieve comprises a material selected from the group consisting of zeolite and MCM 41,
the unsupported solid base catalyst comprises a material selected from the group consisting of an alkaline earth metal exchanged molecular sieve, calcium oxide (CaO), magnesium oxide (MgO), and silicon oxide (SiO₂),
20 the catalytic metal comprises a metal selected from the group consisting of noble metals, non-noble metals, and combinations thereof, and
the metal oxide support comprises a metal oxide selected from the group consisting of a Group IV metal oxide, a Group V metal oxide, a Group IIIA metal oxide, and combinations thereof.
25
2. The process of claim 1, wherein the zeolite is selected from the group consisting of BEA-type zeolite, zeolite X, zeolite Y, zeolite ZSM 5, and zeolite ZSM 12.
3. The process of claim 1, wherein the Group V metal oxide comprises
30 niobium oxide (Nb₂O₅).

4. The process of claim 1, wherein the alkaline earth metal exchanged molecular sieve comprises a molecular sieve selected from the group consisting of barium exchanged molecular sieve and calcium exchanged molecular sieve.

5

5. The process of claim 1, wherein the catalytic metal on the metal oxide support comprises a non-noble metal selected from the group consisting of nickel molybdenum, cobalt, and tungsten or a noble metal selected from the group consisting of platinum, rhodium, ruthenium, palladium, iridium, and combinations thereof.

10

6. The process of claim 1, wherein the metal oxide support comprises a metal oxide selected from the group consisting of titanium oxide (TiO_2), zirconium oxide (ZrO_2), niobium oxide (Nb_2O_5), silicon oxide (SiO_2), and combinations thereof.

15

7. The process of claim 1, wherein the alcohol comprises an aliphatic alcohol selected from a group consisting of methanol, ethanol, propanol, and butanol.

8. The process of claim 1, wherein step of pre-treating the biomass-derived pyrolysis oil comprises reducing a water content of the biomass-derived pyrolysis oil.

20

9. The process of claim 1, further comprising the step of diluting the treated acid-containing biomass-derived pyrolysis oil with ethanol to form a solution of at least 30% ethanol, by weight, before the step of esterifying.

25

10. The process of claim 1, further comprising the step of distilling the low-acid biomass-derived pyrolysis oil to separate ethanol from the low-acid biomass-derived pyrolysis oil.

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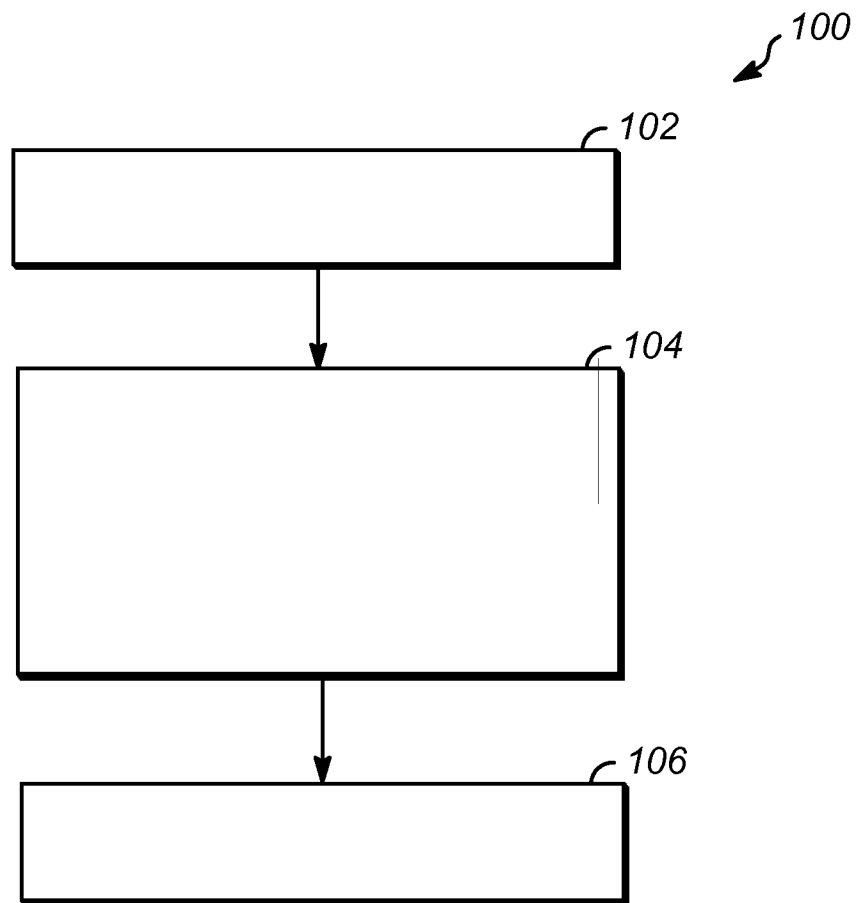


FIG. 1

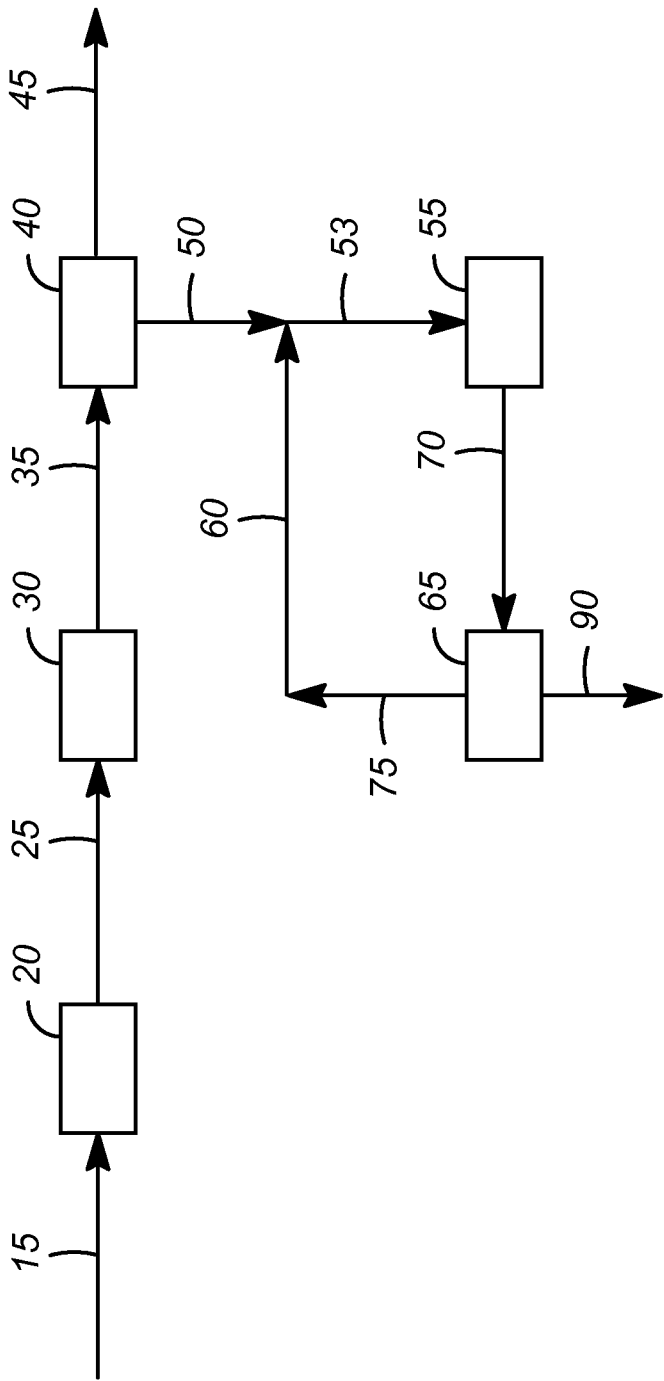


FIG. 2

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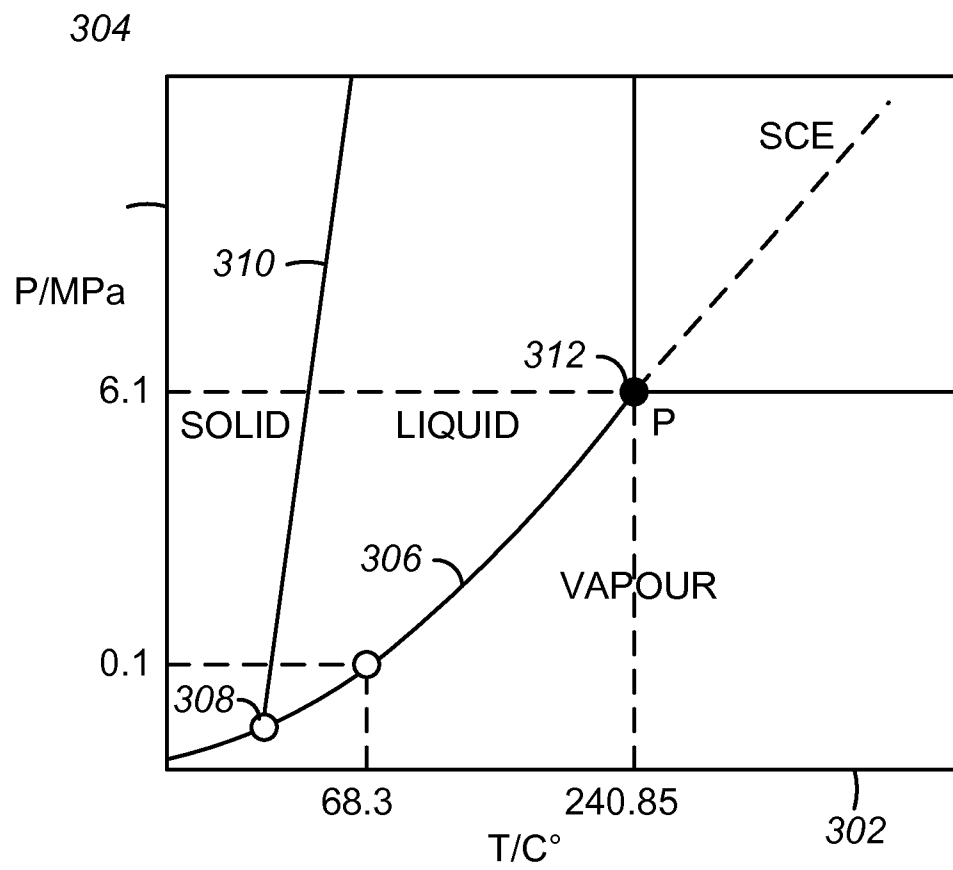


FIG. 3